INL/CRADA-00-03

CRADA FINAL REPORT

RSP Tooling Technology

Idaho National Laboratory

and

Vitro Group

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Vitro/INEEL CRADA Phase I Results

Background:
RSP Tooling™ is a spray forming technology tailored for producing molds and dies. The approach combines rapid solidification processing and net-shape materials processing in a single step. The general concept involves converting a mold design described by a CAD file to a tooling master using a suitable rapid prototyping (RP) technology such as stereolithography. A pattern transfer is made to a castable ceramic, typically alumina or fused silica (Figure 1). This is followed by spray forming a thick deposit of a tooling alloy on the pattern to capture the desired shape, surface texture, and detail. The resultant metal block is cooled to room temperature and separated from the pattern. The deposit's exterior walls are machined square, allowing it to be used as an insert in a standard mold base. The overall turnaround time for tooling is about 3 to 5 days, starting with a master. Molds and dies produced in this way have been used in high volume production runs in plastic injection molding and die casting.

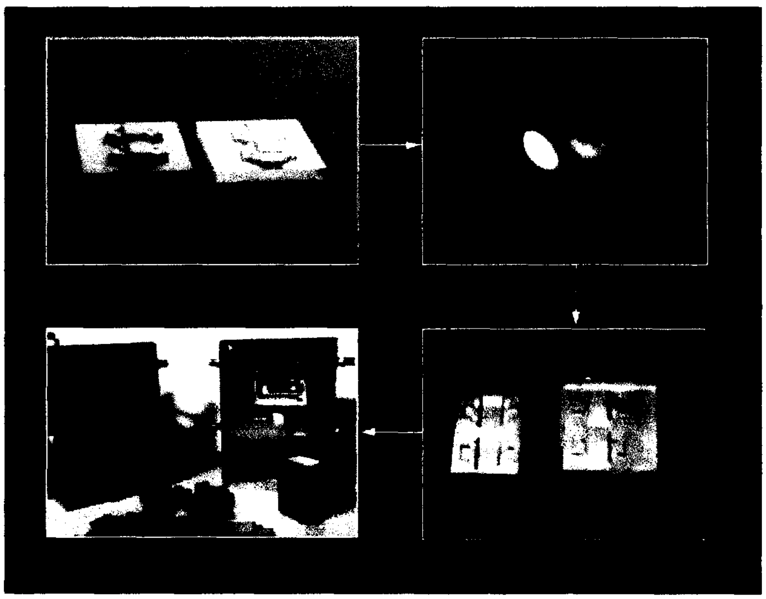

Figure 1. RSP Tooling™ processing steps.

A Cooperative Research and Development Agreement (CRADA) between the Idaho National Engineering and Environmental Laboratory (INEEL) and Grupo Vitro has been established to evaluate the feasibility of using RSP Tooling technology for producing molds and dies of interest to Vitro. This report summarizes results from Phase I of this agreement, and describes work scope and budget for Phase II activities.

Phase I results:
The main objective in Phase I was to demonstrate the feasibility of applying the Rapid Solidification Process (RSP) Tooling method to produce molds for the manufacture of glass and other components of interest to Vitro. This objective was successfully achieved.

During Phase I, Vitro supplied INEEL with gray iron and aluminum bronze stock alloys, and a production metal mold used to produce perfume bottles. The base of the mold was used at INEEL to make similar mold bases in P20 tool steel, aluminum bronze and gray iron following the sequence:

Perfume bottle mold base (supplied by Vitro) → RTV silicone rubber (master) → ceramic tool pattern → duplicate mold base (made using RSP Tooling process)

This sequence is illustrated in Figure 2. The spray-formed mold base is P20 tool steel.

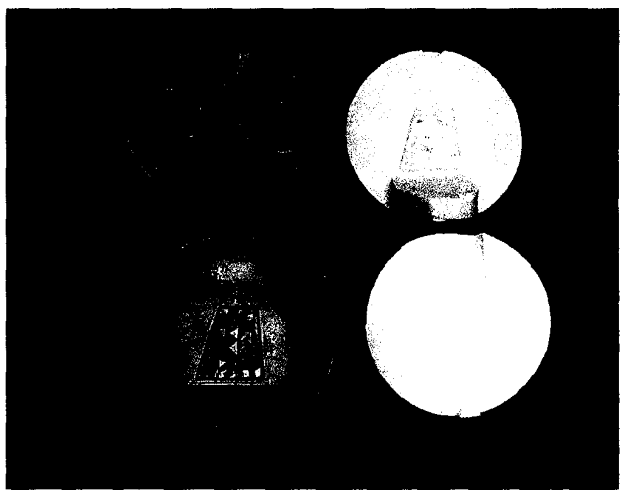

Figure 2. Perfume bottle mold base (upper left); RTV silicone rubber (upper right); ceramic tool pattern (lower right); spray-formed P20 tool steel deposit (lower left).

<u>Results with P20 tool steel:</u>
Spray forming P20 tool steel was straightforward. The tool steel was melted and superheated about 100 ^{o}C above the liquidus temperature (1470 ^{o}C), atomized by contacting the molten metal stream with heated nitrogen gas, and deposited onto a preheated ceramic (alumina) tool pattern. Detail replication of the P20 tool steel deposit, shown in Figure 2, was excellent. Prior microstructure and material property analysis has shown that strength, hardness, machinability, weldability, etc. are comparable to

commercial prehardened P20 tool steel. Production runs of spray-formed P20 tool steel plastic injection molds have been used to manufacture polyethylene, ABS, polypropylene, glass filled nylon, etc. components with a mold life that is comparable to conventional machined molds. Component cycle time is also equivalent to that of a conventional machined mold.

Results with aluminum bronze:

Aluminum bronze alloys supplied by Vitro atomized well using the standard nozzle design for tool steels, yielding a finely atomized spray with an average particle size of approximately 20 microns. In Figure 3, a spray-formed Al-bronze deposit is shown together with an RTV silicone rubber master used to cast ceramic (alumina) tool patterns. As with P20 tool steel, excellent detail replication of features was obtained.

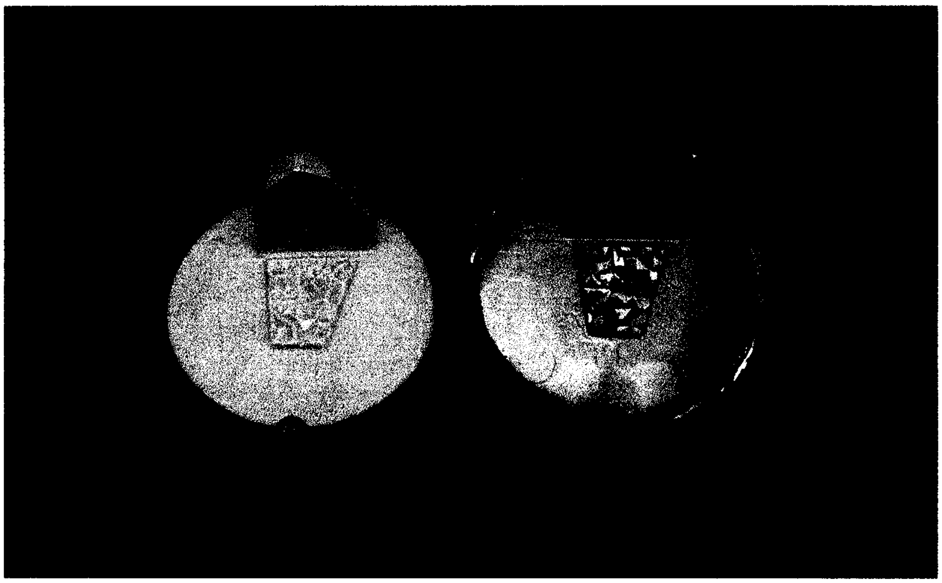

Figure 3. RTV Master (left) and Al bronze insert (right)

Microstructural analysis of cast and spray-formed Al bronze indicated the presence of two phases, one rich in Cu (light) and the other rich in Al (dark) (see Figure 4). The phase distribution in the spray-formed material is significantly more uniform and refined than in the cast alloy due to rapid solidification.

Al bronze metal was melted about 1060 $^{\circ}$C, superheated to about 1160 $^{\circ}$C, and atomized with preheated nitrogen gas. It was immediately evident that the alloy contained a small amount of zinc which evaporated from the atomized droplets during their flight to the substrate producing a dense black smoke. At 1160 $^{\circ}$C, the equilibrium vapor pressure of zinc is very high—about 10 atm. Atomization increases the surface area of the melt by a factor of about 10^{10}, resulting in a high Zn evaporation rate and depletion of Zn from the alloy.

Figure 4. Photomicrographs of Al bronze at the same magnification. Cast (left); spray formed (right). Polished, 500X.

Composition analysis of the Al bronze alloy was performed using Energy Dispersive Spectroscopy (EDS). The spectrograph in Figure 5 verifies the presence of zinc as shown by the small peak to the right of the large Cu peak. This analysis indicated that the alloy contained about 1 wt.% zinc. Composition results are summarized in Table 1.

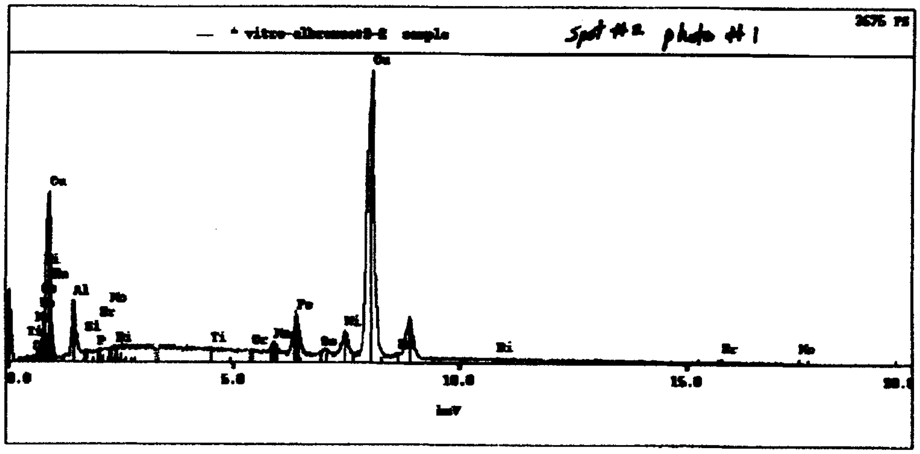

Figure 5. EDS spectrograph of Al bronze alloy supplied by Vitro.

Element	*Wt %*	*Atomic %*
Cu	80.36	73.13
Ni	4.72	4.64
Al	6.61	14.16
Zn	1.02	0.90
Fe	5.02	5.20
Mn	1.09	1.15
Other	1.18	0.82

Table 1. EDS composition analysis of Al bronze alloy supplied by Vitro.

The RSP Tooling process does appear to be suitable for making Al bronze molds for glass manufacture assuming thermal conductivity is adequate and alloys do not contain zinc. It is recommended in Phase II that a zinc-free Al-bronze alloy, such as Exca Eballoy 690, be spray formed and that the thermal conductivity of the spray-formed material be compared with that of the cast material currently used at Vitro.

Results with gray iron:
The thermophysical properties of molten gray iron, such as surface tension and viscosity, differ from those of tool steel. Spray parameters and operating conditions which worked well with P20 tool steel were found to yield less satisfactory results with gray iron, largely due to differences in atomization behavior. In an attempt to produce suitable gray iron deposits, four spray runs were conducted by varying the following conditions:

1. Superheating the molten gray iron 100°C above the liquidus temperature.
2. Increasing the melt superheat to 200°C to lower surface tension.
3. Reducing melt feed rate into the nozzle by ~ 40%, thereby increasing the gas-to-metal mass flow ratio (G/M) to improve atomization efficiency.
4. Increasing the gas flow rate to further increase G/M and atomization efficiency.

Each step resulted in improvement in atomization efficiency and smaller average particle size in the spray. Despite these attempts, gray iron did not atomize as well as P20 tool steel or Al-bronze. Poorer atomization resulted in a relatively large average droplet size, a broader droplet size distribution, and high porosity levels. Using the last set of spray conditions, a gray iron deposit with excellent surface replication, comparable to P20 and Al-bronze, was obtained, as shown in Figure 6. An important aspect of technology development in Phase II will be the development of an RSP Tooling atomizing nozzle optimized for gray iron.

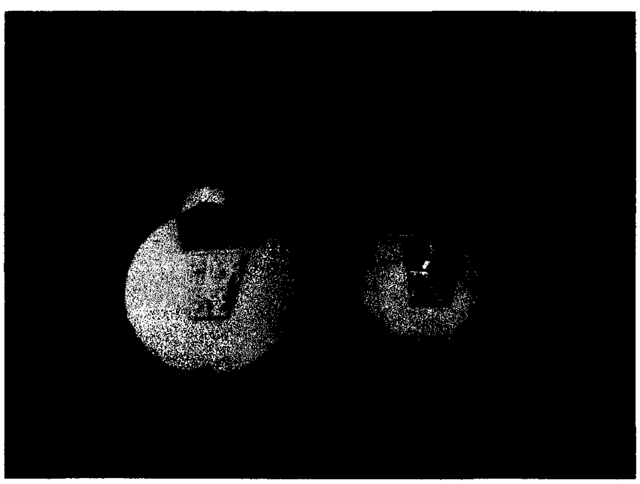

Figure 6. RTV master (left) and gray iron deposit (right).

As-deposited gray iron is harder and stronger than desired. Microstructurally, it consists of a combination of ferrite and pearlite, with relatively small graphite flakes and higher levels of cementite than the cast material (Figure 7). In order to increase thermal conductivity, thermal shock resistance, and improve machinability, a ferrite matrix with relatively large graphite flakes is desirable.

Heat treatment at 700^{O}C, i.e., below the eutectoid transformation temperature, increased flake size slightly (Figure 8).

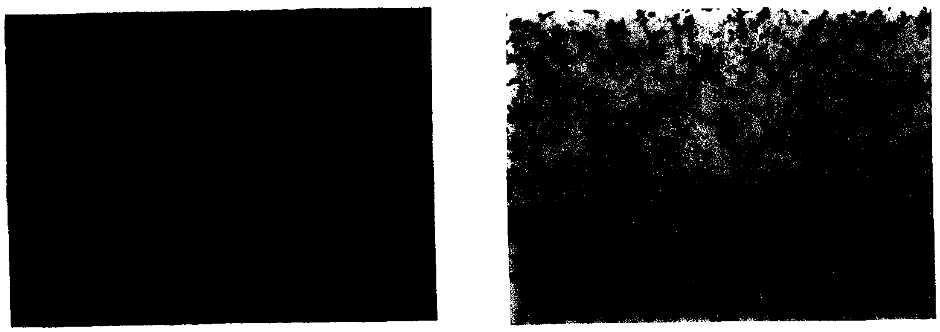

Figure 7. Photomicrographs of gray iron. Cast as supplied by Vitro (left) and spray formed (right). Polished, 500X.

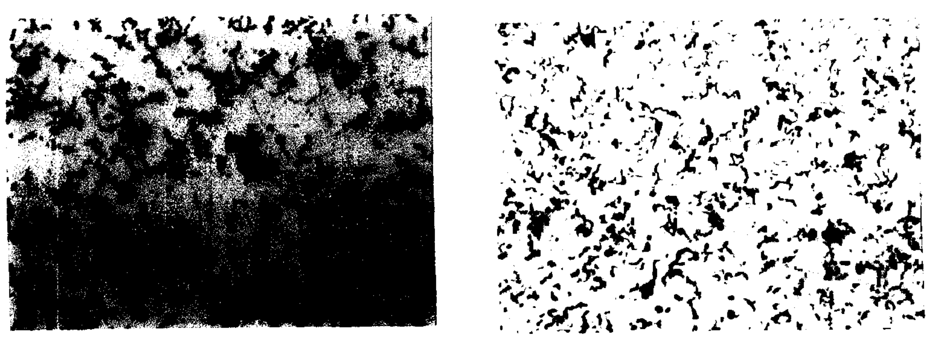

Figure 8. Photomicrographs of spray formed and heat treated gray iron. Spray formed/soaked at 700^{O}C for 3 hrs./quenched (left). Spray formed/slowly heated to 700^{O}C/soaked for 3 hrs./slowly cooled (right). Polished, 500X.

Heat treatment above the eutectoid transformation temperature, however, resulted in desirable decomposition of cementite to graphite and ferrite. Figure 9 compares the microstructures of cast gray iron supplied by Vitro with as-deposited gray iron and spray-formed material following a graphitizing anneal heat treatment. The heat treatment consisted of slowly ramping the furnace temperature to 941°C, holding at temperature for one hour, and slowly cooling the sample to room temperature. After polishing, samples were etched with 2% nital to reveal the nature of the matrix phases. The cast gray consists of relatively large, randomly oriented graphite flakes in a ferrite matrix. Due to the much higher cooling rate that accompanied the spray deposition of gray iron, a combination of fine, randomly oriented graphite flakes, together with fine-grained ferrite, cementite, and pearlite with fine interlamellar spacing, was observed.

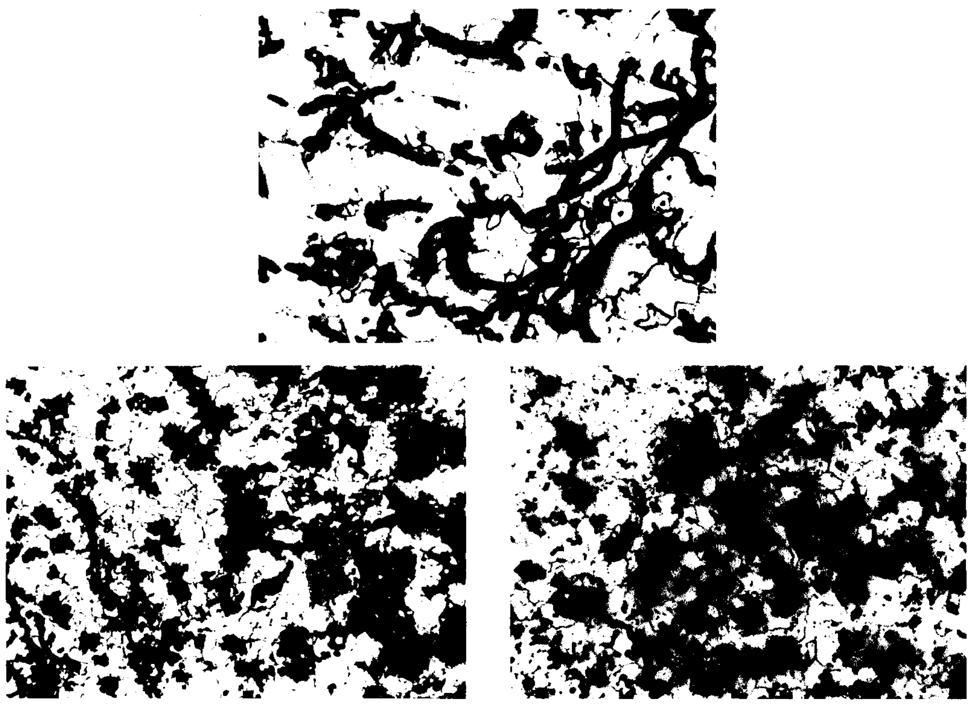

Figure 9. Photomicrographs of cast and spray-formed gray iron. Cast, as supplied by Vitro (upper), spray formed as-deposited (left), spray formed and graphitize annealed (right). 500X, 3% nital.

Vitro/INEEL CRADA Phase II proposal

During Phase I of the project, the feasibility of using RSP Tooling to rapidly make molds for manufacturing glass components was demonstrated. Work in Phase II will focus on the development and demonstration of spray forming technology customized for gray iron and aluminum bronze alloys used by Vitro. Specific tasks, detailed below, will include design and demonstration of an atomizer optimized for gray iron; optimization of post heat treatment of spray-formed gray iron; structure/property analysis of spray-formed gray iron and Al bronze; quantification of process shrinkage factors; and production of gray iron and Al bronze molds. At the conclusion of Phase II, data will be summarized in a final report. With Vitro's permission, INEEL personnel will provide RSP Tooling LLC, the commercializer of the technology, with engineering design drawings and data on alloy processing parameters and post heat treatment recipes which result from this work.

1. Design/construct/test atomizer optimized for gray iron.
Phase I results indicate that the molten metal atomizer designed to produce tool steel molds and dies works well with P20 tool steel (and Al-bronze) but is not well suited for efficiently atomizing gray iron. This is due to differences in thermophysical properties, notably viscosity and surface tension, between the metals. In Phase II, an atomizer will be designed, constructed, and demonstrated which is optimized for atomizing gray iron. This design will provide improved gas/molten metal coupling and atomization efficiency, and improved uniformity in mass and enthalpy distribution of particles exiting the atomizer. These improvements will allow Vitro to routinely produce blank and finish gray iron molds using the RSP Tooling process.

2. Optimize heat treatment of gray iron.
The thermal and mechanical properties of spray-formed alloys can often be varied over a wide range by combining appropriate spray and deposit cooling rate parameters, and post-spray heat treatments. Given the high processing temperatures and rapid cycle times used in manufacturing glass components, thermal shock resistance and thermal conductivity of the tooling alloys is very important. With gray iron, the amount, size, shape and distribution of graphite flakes plays a significant role in determining thermal properties, while the nature of the matrix phase influences machinability. In general, large flakes that are formed in hypereutectic irons enhance resistance to thermal shock by increasing thermal conductivity and decreasing elastic modulus, both of which reduce thermal stress. It is desirable in glass molds that the matrix phase is ferrite with a uniform dispersion of relatively large graphite flakes.

As demonstrated in Phase I, as-deposited gray iron consists of a combination of ferrite, pearlite and cementite. Exposure to high temperatures was found to decompose cementite, and convert pearlite to ferrite, thereby increasing the amount and size of free graphite flakes. Above about 870°C, for each 50°C increment in holding temperature, the rate of carbide decomposition approximately doubles. Therefore, it is advantageous to place spray-formed gray iron into a furnace immediately following deposition while the material is at elevated temperature, rather than allow it to air cool to room temperature. In addition, machinability will be enhanced by cooling slowly through the transformation range. During phase II, a precise thermal recipe needed to transform the microstructure of spray-formed gray iron to the desired phases will be ascertained. This will be accomplished through microstructure and property analysis of blocks of spray-formed gray iron exposed to elevated temperatures for various lengths of time. Use of inoculants such as ferrosilicon to encourage microstructure transformation will also be evaluated if necessary.

method. Hardness and density will also be measured and compared with base material.

4. Analyze shrinkage factors for spray-formed gray iron and Al bronze.
During the RSP Tooling process, droplets cool rapidly (10^3-10^5 K/s) by convection during their flight to the pattern, and a distribution of particle sizes and thermal histories is present in the spray. Shrinkage in the deposits is primarily dictated by the amount of liquid phase undergoing solidification, and can be tailored by varying spray parameters such as nozzle-to-pattern distance, gas-to-metal mass flow ratio (G/M), melt superheat, etc. Solidification in spray-formed deposits is alloy dependent, and differs significantly from a conventional casting due not only to the dramatically different thermal history and thermophysical properties of the rapidly cooled droplets, but also due to the nature of the solidification front present at the deposit.

In another project, accuracy of the various commercial rapid prototyping technologies (stereolithography, selective laser sintering, fused deposition modeling, etc.) is being evaluated using a test model shown in Figure 10. In addition, shrink factors that occur when RTV silicones and ceramics are cast, and H13 tool steel is spray formed, are also being quantified. This is being done to establish a scaling algorithm that can be applied to a mold design for tool steel molds and dies.

Of particular interest to Vitro is the shrinkage that occurs during the spray forming of gray iron and aluminum bronze molds. Using a test model shown if Figure 10, shrink factors for gray iron and aluminum bronze will be determined by spraying a ceramic test model with these alloys and comparing corresponding dimensions with previously measured dimensions on the ceramic using a CMM.

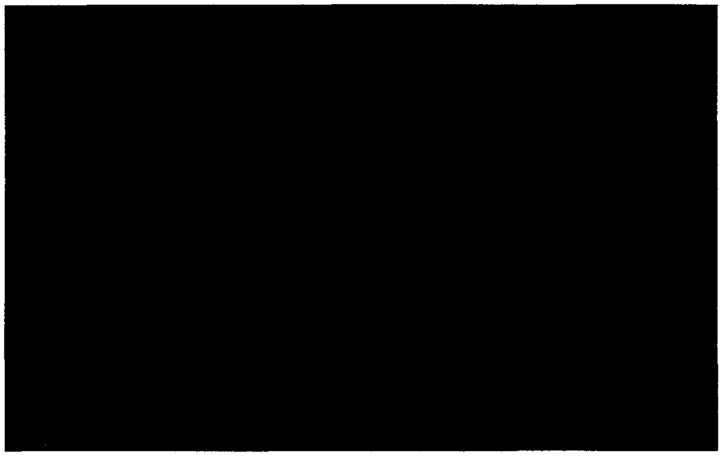

Figure 10. Test model for shrinkage and accuracy evaluation.

5. Produce sample molds for analysis by Vitro.

Using the optimized atomizer design and heat treatment recipe described above, gray iron and Al-bronze molds will be spray formed using the perfume bottle master mold supplied in Phase I. A tooling alloy charge will be melted under an inert gas atmosphere, superheated about 100^{O}C above the liquidus temperature, and pressure-injected into the custom-designed nozzle. There it will be atomized with nitrogen to form fine droplets. The jet will entrain the droplets in a directed flow and deposit them onto a ceramic tool pattern that is manually manipulated in the spray to build an insert about 1”-2” thick. INEEL will supply Vitro with one spray-formed mold of each alloy and representative ceramic patterns.

Budget Requirement (Phase II):

Description	Cost ($K)
Atomizer modification and spray deposition experiments	73.3
Sample analysis	3.7
Materials and supplies	2.5
Travel	4.0
Project management and report	3.5
Total	87.0